

Time Reversal Symmetry breaking superconductivity

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We study time reversal symmetry breaking superconductivity with $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_\alpha$ ($\alpha = s$ or d_{xy}) symmetries. It is shown that the behavior of such superconductors could be *qualitatively* different depending on the minor components (α) and its phase at lower temperatures. It is argued that such *qualitatively different* behaviors in transport and Josephson physics. Orthorhombicity is found to be a *source* of consequences in transport and Josephson physics. Orthorhombicity is found to be a strong mechanism for mixed phase (in case of $\alpha = s$). We show that due to electron correlation the order parameter is more like a pure $d_{x^2-y^2}$ symmetry near optimum doping.

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During last several years, a great deal of effort has been devoted to determine the symmetry of the superconducting order parameter (SCOP) of high T_c cuprate superconductors¹. While there is a strong consensus both from experiments and theory that the symmetry of the SCOP in the cuprates could be $d_{x^2-y^2}$ type; recent studies provide increasing evidence that the pairing symmetry may be an admixture with a minor component, like s , d_{xy} with predominant $d_{x^2-y^2}$ symmetry. The pairing symmetry provides clues to identify pairing mechanism which is essential for the development of the theory of high temperature superconductivity in cuprates, still remains a challenge after a decade of its discovery.

Several different types of measurements which are sensitive to the phase of $\Delta(k)$ indicate a significant mixing of s -wave component with $d_{x^2-y^2}$ symmetry. For example, c-axis Josephson tunnelling studies on junctions consisting of a conventional s wave superconductor (Pb) and twinned or untwinned single crystals of YBCO indicate that the SCOP of YBCO has mixed $d \pm s$ (or $d \pm is$) symmetry^{2,3}. Recently, a new class of c-axis Josephson tunneling experiments are reported by Kouznetsov *et al.*⁴ in which a conventional superconductor (Pb) was deposited across a single twin boundary of a YBCO single crystal. Their measurements of critical current as a function of the magnitude and angle of a magnetic field applied in the plane of the junction provides a direct evidence for mixed d - and s -wave pairing in YBCO. A series of high resolution measurements on thermal conductivity (κ) in the $Bi_2Sr_2CaCu_2O_8$ by Krishna *et al.*⁵ show that the κ at low temperature becomes field-independent above a temperature dependent kink field $H_k(T)$. This remarkable result indicates a phase transition separating a low-field state where the thermal conductivity decreases with increasing field and a high-field one where it is insensitive to applied magnetic field. The authors argue that this phase transition is not related to the vortex lattice because of the temperature dependence of the field $H_k(T)$ (which is roughly proportional to T^2) as well as its magnitude. Instead, they suggest a field-induced electronic transition leading to a sudden vanishing of the quasi-particle contribution to the heat current. Possible scenarios would be the induction of a minor $e^{i\theta} \Delta_\alpha$

($\alpha = d_{xy}$ or s) component with $d_{x^2-y^2}$ symmetry with application of a weak field. A similar conclusion may also be obtained based on the results of angle resolve photoemission spectroscopy (ARPES) experiment by J. Ma *et al.*⁶ in which a temperature dependent gap anisotropy in the oxygen-annealed $Bi_2Sr_2CaCuO_{8+x}$ compound was found. The measured gaps along both high symmetry directions ($\Gamma - M$ *i.e.*, Cu-O bond direction in real space and $\Gamma - X$ *i.e.*, diagonal to Cu-O bond) are non-zero at lower temperatures and their ratio is strongly temperature dependent. This observed feature cannot be explained within a simple d -wave scenario (but is consistent with $d_{x^2-y^2} + e^{i\theta} \alpha$ scenario) and has been taken as a signature of a two component order parameter, $d_{x^2-y^2}$ type close to T_c and a mixture of both s and d otherwise⁷. However, surprisingly enough, the experimental results⁶ was never been reproduced by any other equivalent experiments. In Josephson physics, it was found⁸ that the current-phase relationship depends on the mutual orientation of the two coupled superconductors and their interface (the induced minor component then would be associated with any arbitrary phase, θ). This property is the basis of all the phase sensitive experiments probing SCOP. Therefore, motivated by strong experimental evidences of a mixed order parameter symmetry in high T_c cuprates we present basic behaviors of superconductors with mixed order parameter symmetries such as $d + e^{i\theta} \alpha$, $\alpha = s$, d_{xy} , which is characterized by a local breakdown of time reversal symmetry. A clear evidence will emerge that the time reversal superconductivity at lower temperatures give rise to *unusual* behaviors depending on α and its phase.

Assuming a well defined quasiparticle picture in the superconducting (SC) state, free energy of a superconductor with arbitrary pairing symmetry may be written as,

$$F_{k,k'} = -\frac{1}{\beta} \sum_{k,p=\pm} \ln(1 + e^{-p\beta E_k}) + \frac{|\Delta_k|^2}{V_{kk'}} \quad (1)$$

where $E_k = \sqrt{(\epsilon_k - \mu)^2 + |\Delta_k|^2}$ are the energy eigen values of a Hamiltonian that describes superconductivity. It is generally believed that a single band Hubbard model

contains essential ingredients to describe $Cu - O$ planes where transport processes takes place. Therefore, our model Hamiltonian reads as,

$$\mathcal{H} = H_{HUB} + H_{PAIR} \quad (2)$$

$$H_{HUB} = \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i\sigma} n_{i\sigma} \quad (3)$$

$$H_{PAIR} = \sum_{kk'} V_{kk'} c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger c_{-k'\downarrow} c_{k'\uparrow} \quad (4)$$

where the notations have their usual meanings.

Treatment of the Hubbard on-site correlation is a known problem. We use the Slave Boson theory of Kotliar and Ruckenstein⁹ in which the Hubbard model has solution for any filling and any value of repulsion. The slave - boson formulation of Kotliar and Ruckenstein (KR)⁹ introduces four auxilliary boson fields corresponding to the occupancy of a site, namely empty (e_i), doubly occupied (d_i), singly occupied ($p_{i\sigma}/p_{i-\sigma}$) with spin $\pm\sigma$ respectively. In terms of the slave boson field operators the single band Hubbard model takes the form

$$\begin{aligned} H_{HUB} = & \sum_{ij,\sigma} t_{ij} z_{i\sigma}^\dagger c_{i\sigma}^\dagger c_{j\sigma} z_{j\sigma} + U \sum_i d_i^\dagger d_i - \mu \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} \\ & + \sum_i \lambda_i (1 - e_i^\dagger e_i - d_i^\dagger d_i - \sum_{\sigma} p_{i\sigma}^\dagger p_{i\sigma}) \\ & + \sum_{i\sigma} \lambda'_i (c_{i\sigma}^\dagger c_{i\sigma} - d_i^\dagger d_i - p_{i\sigma}^\dagger p_{i\sigma}) \end{aligned} \quad (5)$$

where $z_{i\sigma} = (1 - d_i^\dagger d_i - p_{i\sigma}^\dagger p_{i\sigma})^{-1/2} (e_i^\dagger p_{i\sigma} + p_{i-\sigma}^\dagger d_i) (1 - e_i^\dagger e_i - p_{i-\sigma}^\dagger p_{i-\sigma})^{-1/2}$ and the Boson field operators are not independent of each other but are constrained by the requirements of completeness and local charge conservation at a site, hence the fourth and fifth terms are added in the Hamiltonian with the help of Lagrange multipliers (λ_i and λ'_i). The values of the boson field operators and Lagrange multipliers are determined by minimizing the free energy in the saddle point approximation. This approximation diagonalizes the U term whereas renormalizes the hopping term as $\tilde{q}t_{ij}$ with $\tilde{q} = z^\dagger z$; \tilde{q} usually being complicated function of u ($= \frac{U}{U_c}$), dopant concentration (δ) and $x(= e + d)$ carries the necessary information of electron correlation. In this approach solutions are obtained for the paramagnetic state for all values of u and band fillings⁷ that reproduces the correct Brinkman-Rice result for metal-insulator transition (U_c) at half-filling.

As a consequence the total Hamiltonian (2) takes the form,

$$\begin{aligned} \mathcal{H} = & \sum_{k\sigma} (\tilde{q}\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma} + \sum_{kk'} \tilde{q}^2 V_{kk'} c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger c_{-k'\downarrow} c_{k'\uparrow} \\ & + \text{bosonic terms} \end{aligned} \quad (6)$$

where the band dispersion $\epsilon_k = \sum_{i=1}^5 C_i \eta_i(k)$ are obtained from the angle resolved photoemission spectroscopy (ARPES) results¹⁰ on $Bi_2Sr_2CaCuO_8$. In de-

veloping Hamiltonian (6) fluctuations of the bose-field operators are *not* considered (consequence of on-site correlation has shown up in (6) as $\epsilon_k \rightarrow \tilde{q}\epsilon_k$ and $V_{kk'} \rightarrow \tilde{V}_{kk'} = \tilde{q}^2 V_{kk'}$).

A mean field superconducting (SC) order parameter $\Delta^*(k) = \sum_{k'} \tilde{V}_{kk'} < c_{k'\uparrow}^\dagger c_{-k'\downarrow}^\dagger >$ allows to solve the Hamiltonian (6) exactly to find the energy eigen values E_k and hence minimization of the free energy (1) (i.e $\partial F_{k,k'}/\partial \Delta_k = 0$) will result the superconducting (SC) gap equation as,

$$\Delta_k = \sum_{k'} \tilde{V}_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \tanh\left(\frac{\beta E_{k'}}{2}\right), \quad (7)$$

where the pairing potential $V_{kk'}$ for a two component order parameter with a separable form and the corresponding gap functions are obtained as,

$$V_{kk'} = \sum_{j=0}^1 V_j f_k^j f_{k'}^j \quad \& \quad \Delta_k = \sum_{j=0}^1 e^{j(i\theta)} \Delta_j f_k^j \quad (8)$$

For a mixed $d_{x^2-y^2} - d_{xy}$ symmetry, $V_{0(1)} \equiv V_{d_{x^2-y^2}} (V_{d_{xy}})$ and $f_k^{0(1)} \equiv \cos k_x - \beta' \cos k_y (2 \sin k_x \sin k_y)$ and the corresponding gap amplitudes are $\Delta_{0(1)} \equiv \Delta_{d_{x^2-y^2}} (\Delta_{d_{xy}})$ ($\beta' \leq 1$ corresponds to orthogonal or tetragonal symmetry). Similarly for a mixed $d_{x^2-y^2} - s$ symmetry, $V_1 \equiv V_s$, $f_k^1 \equiv \text{constant}$ and $\Delta_1 \equiv \Delta_s$. Substituting equation (8) in (7) the gap equations for different components can be separated out as,

$$\Delta_j = \sum_k V_j \frac{\Delta_j f_k^{j2}}{2E_k} \tanh\left(\frac{\beta E_k}{2}\right) \quad (9)$$

The two coupled gap equations (9), a number conserving equation to fix chemical potential (μ) and a sixth order algebraic equation in $x(= e + d)$ (to get correct values of \tilde{q} for any value of u , δ) are solved self-consistently for a fixed cut-off parameter $\Omega_c = 500$ K around the Fermi level beyond which SC pairing does not exist.

In figures 1(a,b) phase diagrams of superconductors with $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \alpha$ where $\alpha = \Delta_{xy}(k)$ (a) and $= \Delta_s$ (b) are obtained for a fixed band filling $\rho = 0.80$ and in a tetragonal square lattice. The phase diagrams comprises the amplitudes of pair condensates, evaluated at 5 K, in different channels as a function of the ratio $\gamma = V_{d_{x^2-y^2}}/V_\alpha$. The minor components α appear at the same value of γ irrespective of the phase θ in the predominant $d_{x^2-y^2}$ phase. But the rate of growth of the minor component is different depending on θ . For $\theta = 0$ i.e for a real order parameter with (a) $d_{x^2-y^2} + d_{xy}$ or (b) $d_{x^2-y^2} + s$ wave symmetry, both the minor as well as the $d_{x^2-y^2}$ component increases with decrease in γ , thereby inducing each other. In case of $d + s$ symmetry this phenomena is very pronounced. However, for any finite $\theta(\neq 0)$ the $d_{x^2-y^2}$ component is suppressed with the enhancement in the isotropic s component at some values

of γ depending on θ resulting in a pure s -wave phase. This feature is absent in $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_{xy}(k)$ scenario.

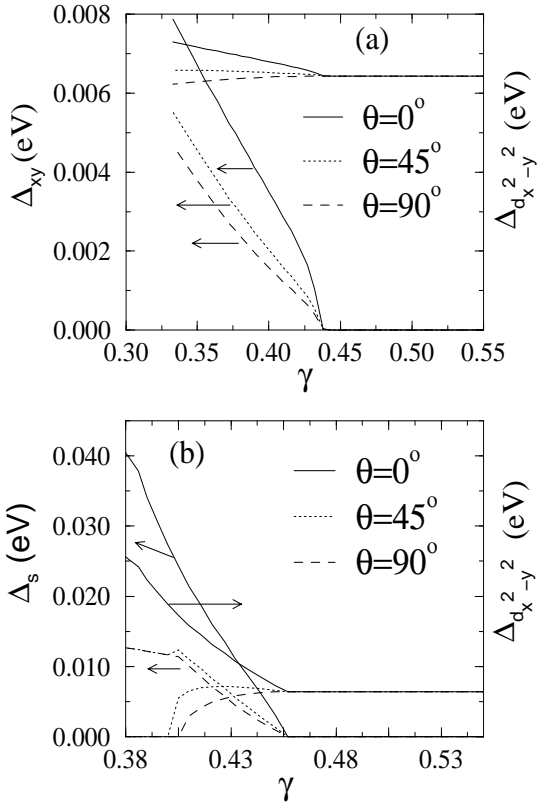


FIG. 1. Phase diagrams of superconductors with (a) $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_{xy}(k)$ and (b) $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_s$ symmetries. Amplitudes of the $d_{x^2-y^2}$, d_{xy} - and s -wave pairing condensates (at 5 K) are plotted as a function of the ratio of pairing strengths in the respective channels, $\gamma = V_{d_{x^2-y^2}}/V_{d_{xy}}$ for $u = 0.4$. Note the *qualitative difference* in (a) & (b); the onset of s -wave component influences the $d_{x^2-y^2}$ -amplitude very strongly (suppresses or enhances depending on the phase θ) whereas the onset of d_{xy} component have no influence on the $d_{x^2-y^2}$ -amplitude except for $d_{x^2-y^2} + d_{xy}$ phase.

For $\pi/2 < \theta < 0$, the minor component has two parts, real and complex (thereby giving rise to most probable mixing), that couples to the $d_{x^2-y^2}$. A close look to figure 1 therefore, would suggest that the mixing of a minor real s or d_{xy} component will stabilize the $d_{x^2-y^2}$ symmetry, whereas inclusion of complex minor component s -wave tends to suppress $d_{x^2-y^2}$ gap. The d_{xy} minor component with a complex phase has hardly any influence on the $d_{x^2-y^2}$ symmetry. These *qualitatively different* behaviors in different classes of mixed order parameter symmetries are also responsible for so with respect to thermal dependency.

It is evident from figures 2(a,b) (for $\rho = 0.8$) that at lower temperatures the minor component plays a signifi-

cant role to the predominant d -wave. For example, when the minor component mixes with the d -wave with a real coefficient (*i.e.*, $\theta = 0$), the minor component has a very fast growth with lowering in temperature and it always *induces* the d -wave component by further stabilizing it. On the other hand, mixing of the minor component with a complex coefficient (*i.e.*, $\theta = 90^\circ$) suppresses the d -wave component when the minor component is s -wave and has no effect when the same is d_{xy} . These behaviors are *bound* to have immense influence on thermodynamic quantities which are sensitive to the thermal gradient of the SC-gap. For instance, the specific heat will then have two jumps, at T_c and at $T_c^\alpha < T_c$ where the minor component (α) vanishes and the nature of the *second* jump can be very different depending on the phase θ providing signature of a true *second* transition below T_c ¹¹.

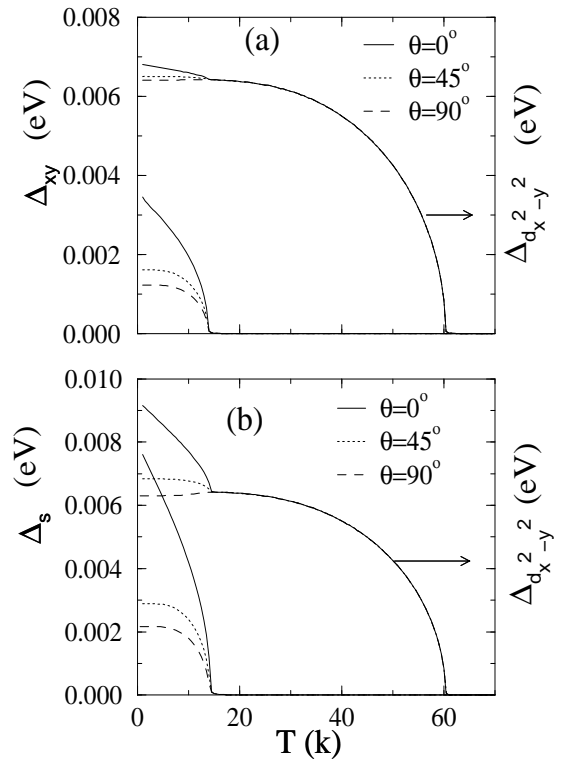


FIG. 2. Thermal behavior of superconductors with (a) $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_{xy}(k)$ ($\gamma = 0.195$) and (b) $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_s$ ($\gamma = 0.18$) symmetries for various values of θ ($u = 0.4$). The minor (s or d_{xy}) component although have *same* T_c their thermal growth inside the d -component is *qualitatively* different. Consequently, the predominant d component is influenced (e.g, further stabilised for $\theta = 0$ and suppressed for $\theta = 90$) very *differently*.

In figures 3(a,b) we present the angular correlation between the amplitudes of different channels evaluated at 5 K and $\rho = 0.8$. For any finite mixing of the minor component with $d_{x^2-y^2}$ -wave thus produces states that

spontaneously breaks time reversal symmetry. Further interesting point to note is that with small orthorhombicity $\beta' = 0.98$, (in the lattice as well), the s component gets enhanced largely (curves with solid circle symbol) whereas the change in d -component with orthorhombicity is rather dependent on θ . For example, the predominant d -component increases with orthorhombicity for $0 < \theta < 0.22\pi$ or $1.78\pi < \theta < 2\pi$ and decreases otherwise (both cases being small, cf. Fig 3(a)). The corresponding changes in $\Delta_{d_{xy}}$ and associated change in $\Delta_{d_{x^2-y^2}}$ are negligibly small (cf. Fig. 3(b)) for such orthorhombicity. Therefore, orthorhombicity could be an intrinsic mechanism for d & s mixing (with an arbitrary phase between them), $d + s$ state being most favorable.

In figures 4(a,b) we demonstrate the role of electron correlation on mixed pairing symmetry. It is shown that the minor component is always minimum at the optimum doping and is suppressed largely due to electron correlation explaining the novel features observed in ARPES experiment¹². This is based on the study of the amplitudes of the different components for the case of $\theta = \pi/2$ (*i.e* $d+is$ state) and for fixed $T_c^\alpha = 45K$ at $u = 0$ as a function of density $\rho (=1-\delta)$. The amplitudes are normalized with respect to the value of the d -component at optimum doping (the d -wave also gets suppressed with u but at a slower rate). Note, the electronic correlation suppresses the minor component very largely close to half-filling

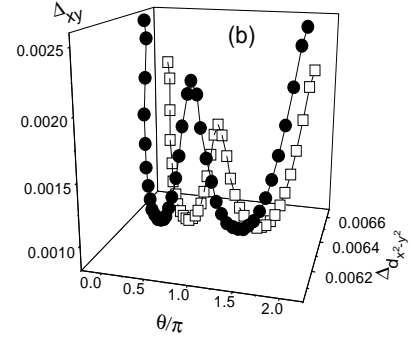
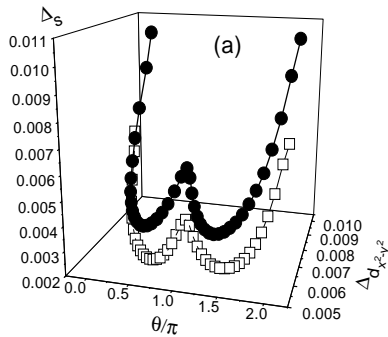


FIG. 3. Amplitudes of the $d_{x^2-y^2}$ and the minor gap (a) s or (b) d_{xy} as a function of the phase of the minor component (for $u = 0.4$ & $T_c^\alpha = 14K$). The curves with solid circles represent orthorhombic phase with $\beta' = 0.98$ whereas the curves with open squares correspond to tetragonal lattice.

whereas hardly have any effect at lower densities (the d -wave boundary shrinks a bit). Also, this behavior with density is similar for any other arbitrary value of θ ¹¹. Apparently, therefore, close to the optimum doping the order parameter will be more like a pure $d_{x^2-y^2}$ like. Furthermore, no mixing is found within a wide range of densities between d -wave with other probable minor components like $s_{x^2+y^2}$, s_{xy} (*e.g*, these components have maxima at $\rho \sim 0$)

Therefore, we have presented basic consequences of time reversal symmetry breaking superconductivity. It is demonstrated that mixing of a minor component at lower temperatures can give rise to *unusual* thermal behaviors depending on the nature of the minor component as well as the phase associated with it. In the *fully gapped* phase at lower temperatures, as described by the $\Delta_k = \Delta_{x^2-y^2}(k) + e^{i\theta} \Delta_\alpha$ scenario, the number of quasi-particles will be exponentially small and hence will contribute negligibly small to thermal conductivity (and in any other transport properties). This scenario therefore can justify the experimental observation by Krishna *et al.*,^{5,7}. This scenario also has strong potential to have natural explanation to the experimental observation⁴ as discussed earlier, because mixing of a minor component (s or d_{xy}) with predominant $d_{x^2-y^2}$ wave would change sign across the twin boundary (hence the situation is described in figures 3) yielding a dramatically different angular dependence.

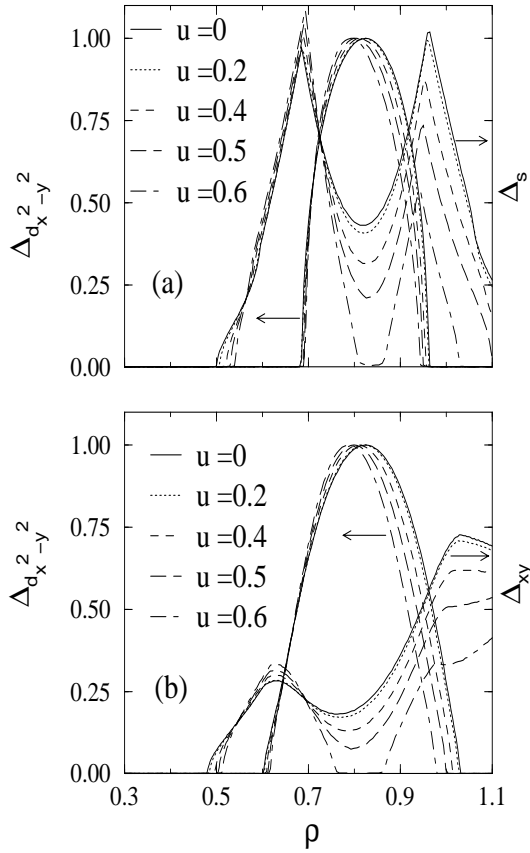


FIG. 4. Amplitudes of different components of (a) $\Delta_k = \Delta_{x^2-y^2}(k) + i\Delta_s$ and (b) $\Delta_k = \Delta_{x^2-y^2}(k) + i\Delta_{xy}$ superconductors at 5K. The minor (s or d_{xy}) component at $u = 0$ has $T_c^\alpha(0) = 45K$. The electron correlation minimizes the mixing of the minor component at optimum doping.

In particular, this study provides a significant understanding on the nature of thermodynamic transition to a gapped or coherent phase from an ungapped or incoherent phase. We also pointed out the subtle role of electronic correlation with number density prohibiting mixing of the minor component at optimum doping.

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